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# Hydrogenation of benzoic acid to benzyl alcohol over Pt/SnO<sub>2</sub>

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Graphical abstract



# Partial reduction of SnO<sub>2</sub> at interface with Pt activates the acid carbonyl group

### Highlights

- Highly selective hydrogenation of benzoic acid to benzyl alcohol over Pt/SnO<sub>2</sub>
- Aromatic ring hydrogenation hindered by alloy phases/migration of  $SnO_x$  onto Pt
- Acid carbonyl group activated by oxidised tin species at periphery of Pt particles
- The interaction between Pt and SnO<sub>2</sub> depends on temperature of reduction
- DFT modelling: switch in adsorption mode of benzoic acid with support reduction

### Abstract

Hydrogenation of benzoic acid in the liquid phase over  $Pt/SnO_2$  has afforded excellent selectivity to benzyl alcohol under mild reaction conditions (97% at 98% conversion of benzoic acid). DFT calculations have shown that the favoured mode of adsorption of benzoic acid switched from the aromatic ring to the acid carbonyl group with

partial reduction of the SnO<sub>2</sub> support. The switch in adsorption mode corroborates the experimentally observed selectivity with acid carbonyl group adsorption and hydrogenation occurring over Pt/SnO<sub>2</sub>. Reduction of Pt/SnO<sub>2</sub> was observed by in-situ XPS forming a degree of metallic tin and complete reduction of Pt which could lead to Pt-Sn alloy phases and/or migration of SnO<sub>x</sub> onto Pt blocking sites for ring hydrogenation. No hydrogenation of benzene or the benzene ring of benzoic acid was observed over Pt/SnO<sub>2</sub> with oxidic tin species at the interface of Pt particles proposed to activate the acid carbonyl group for hydrogenation.

### Keywords:

Benzoic acid, benzyl alcohol, selective hydrogenation, DFT, ATR-IR

### 1 Introduction

There is continuing interest in the development of heterogeneous catalysts for the selective hydrogenation of carboxylic acids to form alcohols as platform chemicals and intermediates in the production of fine chemicals and pharmaceuticals.[1] Hydrogenation of saturated carboxylic acids and fatty acids in the liquid phase to the corresponding alcohols has been reported over Ru, Pt and Re based catalysts predominantly supported on reducible metal oxides such as TiO<sub>2</sub>.[1-4] However, to chemoselectively hydrogenate the carbonyl group in an acid containing additional and more reactive functionality presents an additional challenge.

Pd-Re/graphite catalysts have shown ability for hydrogenation of a range of acid substrates to either alcohols or alkanes through control of the reaction conditions. Reactions at 130 °C/20 bar H<sub>2</sub> formed the corresponding alcohol while reaction at 160 °C/30 bar H<sub>2</sub> lead to an alkane product[5]. This catalyst showed high yields of alcohols from aliphatic acids and diols from diacids; however, for unsaturated acids containing aromatic rings or C=C bonds (benzoic acid, furoic acids, oleic acid (isolated C=C) and 9-decyncaeboxylic acid (isolated C=C)) reaction of the unsaturated functionality in addition to the acid carbonyl group occurred. Of note is that separation of the aromatic ring from the acid functionality in the substrate, as in phenylacetic acid, provided high selectivity to the aromatic alcohol product.

Phenylethanol was formed with a yield of 73% with no aromatic ring hydrogenation observed. In addition, cinnamic acid showed reaction of the C=C and acid carbonyl groups to form phenylpropanol with the aromatic ring left intact. This was attributed to rapid reaction of the C=C group to yield phenylpropanoic acid which as for the non-conjugated phenylacetic acid gave only reaction of the carboxylic acid group.

Unsaturated carboxylic acid hydrogenation has also been reported over Re/TiO<sub>2</sub> at 140°C/50 bar H<sub>2</sub> where acid hydrogenations proceeded without reaction of the aromatic ring for substrates such as phenylpropanoic acid [4, 6]. Interestingly, it was found that Re/TiO<sub>2</sub> did have an ability to hydrogenate an aromatic ring as was demonstrated with the reaction of propylbenzene to propyl cyclohexane; however, this reaction did not occur when in the presence of an acid or alcohol. This suggests stronger adsorption of acids/alcohols compared to aromatic rings on Re which was also evidenced from DFT calculations on Re(001) and ReOx surfaces which showed relatively weaker adsorption of benzene and stronger adsorption of acetic acid compared to Pd(111) and Rh(111) surfaces where benzene was adsorbed more strongly [4]. For aromatic carboxylic acids, the higher affinity of Re and ReOx surfaces towards adsorption of the acid carboxyl group provides a highly selective reaction for acids such as phenylpropanoic acid. However, of note is that high selectivity towards acid carbonyl hydrogenations for substrates where the acid carbonyl group was conjugated with an aromatic ring, as in benzoic acid, was not observed over PdRe/graphite (not tested for Re/TiO<sub>2</sub>). Hydrogenation of benzoic acid over PdRe/graphite formed cyclohexylmethanol with a 72% yield showing the ease of aromatic ring hydrogenation of this substrate compared to phenylacetic acid.

The selective hydrogenation of benzoic acid to cyclohexane carboxylic acid has been shown to proceed with excellent selective towards the hydrogenation of the aromatic ring being achieved under very mild reaction conditions, [7-12] whilst PdReTiO<sub>2</sub> (130 °C and 20 bar H<sub>2</sub>) and Rh/Al<sub>2</sub>O<sub>3</sub> based catalysts (150 °C and 100 bar H<sub>2</sub>) resulted in complete reduction to the saturated alcohol. [5, 13] (Scheme 1). High selectivity to benzyl alcohol has been achieved homogeneously [14, 15] and in the gas phase over Au supported on CeO<sub>2</sub> and Ce<sub>0.62</sub>Zr<sub>0.38</sub>O<sub>2</sub> catalysts at 250-300 °C with the concentration of oxygen vacancies in the supports influencing direct or sequential pathways to benzyl alcohol.[16] The nature of the metal and support influences the activity and selectivity in the hydrogenation of benzoic acid [17]; however, to date, there are few studies where both high activity and high selectivity to benzyl alcohol have been reported showing that selective hydrogenation of the benzoic acid to benzyl alcohol is still a challenging reaction over heterogeneous catalysts.



Scheme 1: Hydrogenation pathways of benzoic acid.

The highest selectivity reported, to date, for the liquid phase hydrogenation of benzoic acid was over a Ru based catalyst with the addition of tin as a promoter of selectivity [18]. Tin has also been used as a promoter of selectivity for Ru and Rh based catalysts for the chemoselective hydrogenation of the unsaturated carboxylic acid oleic acid[19, 20] and for selective C=O hydrogenation in  $\alpha$ , $\beta$ -unsaturated aldehydes[21-23].

For benzoic acid, Ru-Sn/Al<sub>2</sub>O<sub>3</sub>, with 5% Ru with 11.7% Sn, prepared by sequential impregnation (Sn addition to alumina with calcination before addition of the Ru precursor) with optimal activity found for the catalyst following high temperature calcination (973 K) and reduction (723 K), afforded benzyl alcohol in 94% yield for reaction at 260 °C and 98 bar H<sub>2</sub> (selectivity quoted after 6 h of reaction). The interaction between Pt and Sn has been reported to enhance catalytic activity and selectivity for Pt-Sn based catalysts with metal precursor, catalyst preparation method and reduction temperature all shown to influence the nature and degree of interaction formed between Pt and Sn[24].

Herein, we report the chemoselective hydrogenation of benzoic acid over a  $Pt/SnO_2$  catalyst prepared by a standard wet impregnation method. Pt supported on  $SnO_2$  catalysts have been shown to improve the selectivity to C=O

hydrogenation for  $\alpha\beta$ -unsaturated aldehyde crotonaldehyde where formation of PtSn alloy phases were proposed to be important for activity and selectivity of the catalyst [21]. Increased activity for crotonaldehyde hydrogenation was also observed for PtSn/C catalysts where alloy formation and oxidised tin species were proposed to provide the selectivity enhancement with alloy formation / dilution of the Pt surface proposed to hinder C=C bond hydrogenation while oxidised tin species activated the C=O group for hydrogenation [22].

In this study we report the selective hydrogenation of benzoic acid to benzyl alcohol over  $Pt/SnO_2$  under significantly milder conditions, 190 °C and 30 bar H<sub>2</sub>, than has been reported, to date, with no ring hydrogenation products observed.

### 2 Materials and methods

#### 2.1 Catalyst preparation and characterisation

Both 5%Pt supported on alumina and tin(IV) oxide catalysts were prepared by wet impregnation. Platinum (IV) nitrate (Alfa Aesar) precursor was added to  $\gamma$ -aluminium oxide (255 m<sup>2</sup>g<sup>-1</sup>, Alfa Aesar) or SnO<sub>2</sub> (6.70 m<sup>2</sup>g<sup>-1</sup>, Aldrich) in a methanol solution and the mixture stirred for 12 h. After the solvent was evaporated, the paste was dried in air for 4 h at 120 °C and then calcined in air for 4 h at 500 °C. Pt/C (10 wt% Pt) was purchased from Sigma.

The surface area, total pore volume and average pore diameter of the synthesised catalysts were measured by N<sub>2</sub> adsorption-desorption isotherms at 77 K using Micromeritics ASAP 2020. The pore size was calculated on the adsorption branch of the isotherms using Barrett-Joyner-Helenda (BJH) method and the surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The composition of these catalysts was determined using a Perkin Elmer Optima 4300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The metals were digested from the oxide supports using nitric acid and hydrochloric acid.

The powder X-ray diffraction technique was used for the characteristics of the crystalline structure of catalysts, with a PANalytical X'Pert Pro MPD X-ray diffractometer using Cu K<sub> $\alpha$ </sub> irradiation. The diffractograms were measured from 20 to 80° (20), with a step size of 0.033° (20).

H<sub>2</sub>-TPR measurements were carried out using a Quantachrome ChemBet Pulsar TPR/TPD, equipped with a thermal conductivity detector (TCD). Prior to the TPR measurement, approximately 20 mg of the respective catalysts was loaded into a quartz U-tube plugged with quartz wool. The sample was pre-treated under 10% O<sub>2</sub>/He at 350 °C for 60 min at a total flow of 40 cm<sup>3</sup>·min<sup>-1</sup> and the temperature was then decreased to -50 °C, where 5% H<sub>2</sub>/Ar was introduced at the same flow rate. The temperature was then increased from -50 to 800 °C at 10 °C·min<sup>-1</sup>.

CO chemisorption measurements were carried out using a Quantachrome ChemBet Pulsar TPR/TPD, equipped with a thermal conductivity detector (TCD). Prior to the adsorption of CO, the Pt/Al<sub>2</sub>O<sub>3</sub> or Pt/SnO<sub>2</sub> (30 mg) was reduced at either 200 or 350 °C under 5%H<sub>2</sub>/Ar at a total flow of 40 cm<sup>3</sup>·min<sup>-1</sup>. After reduction, the system was purged with He and the temperature lowered. The adsorption of CO was performed at -60 °C with the catalysts exposed to pulses of 10% CO/He repeatedly until no further uptake was observed.

Transmission electron microscope (TEM) images, scanning transmission electron microscope (STEM) images and energy dispersive X-ray spectroscopy (EDS) spectrum images were obtained with an FEI Talos F200X microscope equipped with an X-FEG electron source and Super-X SDD EDS detectors. The experiment was performed using an acceleration voltage of 200 kV and a beam current of approximately 1 nA. TEM images were recorded with an FEI CETA  $4k \times 4k$  CMOS camera. STEM images were acquired with a HAADF detector.

Near ambient pressure (NAP) X-ray photoelectron spectroscopy (XPS) was carried out on a Specs DeviSim NAP system (base pressure  $1 \times 10^{-9}$  mbar). The photoelectrons were excited using a monochromated Al-K $\alpha$  (1486.6 eV) source which was micro focused to a 300 µm spot with analysis of the photoelectrons carried out using a Specs Phoibos 150 differentially pumped electron analyser operating at 30 eV pass energy.

The 5% Pt-SnO<sub>2</sub> powder was mounted to a gold foil substrate support prior to loading into the vacuum environment. NAP-XPS analysis, H<sub>2</sub> exposure and temperature treatments were carried out in a highly controlled fashion within the Specs DeviSim NAP cell which was docked onto the first differential aperture of the Phoibos analyser during analysis.

XPS spectral fitting and analysis was carried out using Aanalyzer software in conjunction with CasaXPS. Spectra were fitted using Voigt profiles (with the exception of metallic species which were fitted using asymmetrical line shapes) utilising Shirley backgrounds. All spectra were charge corrected to the gold foil substrate signal (Au4f<sub>7/2</sub> at 84 eV) with the minor adventitious carbon signal also noted to remain at the accepted value of 284.8 eV throughout the course of the analysis.

Reduction of the metal oxide species was carried out by flowing hydrogen into the NAP cell up to a pressure of 1 mbar and subsequently raising the sample temperature from room temperature (~300 K) to 475 K during hydrogen flow where it was held at this target temperature for 15 minutes.

DRIFT spectra were recorded over the catalyst using a Bruker Tensor 27 FTIR spectrometer with a Spectra Tech Collector II DRIFTS accessory with environmental chamber allowing spectra to be recorded under gas environments and at elevated temperatures.[25] The Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/SnO<sub>2</sub> catalysts were reduced at reduction temperatures between 100 and 350 °C for 1 h in 10%H<sub>2</sub> in Ar. The gas feed was then switched to Ar to purge the cell before cooling to room temperature for the adsorption of CO (2% CO in Ar, 50 mL·min<sup>-1</sup>). Spectra were recorded with 128 scans at 4 cm<sup>-1</sup> and the background was the fresh catalyst before reduction.

ATR-IR spectra were recorded over alumina and Pt/Al<sub>2</sub>O<sub>3</sub> layers slurried onto a ZnSe crystal in water. Spectra were recorded using a PIKE ATRMaxII accessory housed in a Bruker Tensor II spectrometer. All layers were initially heated to 90 °C under a flow of hydrogen saturated dioxane for 30 min before cooling and switching to 0.1 M benzoic acid in dioxane solution. Spectra were recorded with 8 scans at 4 cm<sup>-1</sup> resolution and the background was the fresh catalyst layer before introduction of solvent.

#### 2.3 Hydrogenation reactions

All hydrogenation reactions were performed in a 100 mL Parr batch reactor and the typical reaction conditions were 0.002 mol substrate (benzoic acid or benzene) in 40 mL 1,4-dioxane, 190 °C and 30 bar  $H_2$  (30 bar total reaction pressure for reaction at

190 °C with a partial pressure of  $H_2$  of 20 bar) over 100 or 200 mg of the respective catalysts with the reaction stirred at 1500 rpm. In addition, reactions at varied  $H_2$ partial pressures (5-20 bar) and concentration of benzoic acid (0.001-0.003 mol) were also performed. Before each reaction, the catalyst was pre-reduced *in situ* for 1 h at 200 °C at 30 bar  $H_2$  in dioxane. Additional reactions following a gas phase reduction of the Pt/SnO<sub>2</sub> catalyst under a flow of  $H_2$  at 200 °C and 400 °C were performed. The flow reduction at 200 °C was performed in the Parr autoclave with no solvent for 1 hour after which 40 ml of benzoic acid solution (0.05 M) was syringed into the reactor through the liquid sampling port while still under  $H_2$  flow. The reactor was then purged with  $H_2$  and the reaction performed (100 mg Pt/SnO<sub>2</sub>, 30 bar  $H_2$  and 190 °C). The reduction at 400 °C for 1 hour was carried out in a furnace under a flow of  $H_2$ . After the reduction, the furnace temperature was lowered and the system purged with  $N_2$  before rapid transfer to the autoclave for reaction again performed at 30 bar  $H_2$  and 190 °C.

Samples were taken from the reactor at different time intervals and analysed by gas chromatography to monitor the compositional change with reaction time and a mass transfer study was performed to ensure that reactions were under intrinsic kinetic control. The gas chromatograph used for composition analysis of the reaction samples was a Perkin Elmer Clarus 500 with a Phenomenex Zebron ZB-WAX capillary column, utilising an FID. Calibration curves for benzoic acid and products benzaldehyde, benzyl alcohol, benzyl benzoate and cyclohexylcarboxylic acid were performed to allow quantitative analysis of the reactions with determination of the reaction mass balance.

The recycle experiment was performed with 0.002 mol substrate in 40 mL 1,4dioxane, 30 bar H<sub>2</sub> and 190 °C, over 200 mg of the catalyst with the reaction stirred at 1500 rpm. The catalyst was recovered by filtration, washed with dioxane and dried in air. Before each reaction, the recovered catalyst was re-reduced as for the first reaction (200 °C for 1 h under 30 bar H<sub>2</sub>). In addition, a recycle experiment whereby the catalyst did not undergo reductive regeneration between reactions was performed. The first reaction ran for 4 hours before the reaction was stopped and the liquid removed before addition of dioxane and 0.002 mol of benzoic acid and a reaction at 190 °C and 30 bar H<sub>2</sub> performed for a second time.

### 2.4 DFT calculations

DFT calculations were carried out with a periodic slab model using the Vienna *ab initio* simulation program (VASP).[26-29] The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE)[30] exchange-correlation functional. The projector-augmented wave (PAW) method [31, 32] was utilized to describe the electron-ion interactions, and the cut-off energy for the plane-wave basis set was 450 eV. Furthermore, to illustrate the long-range dispersion interactions between the adsorbates and catalyst surfaces, we employed the van der Waals density functional (vdW-DF) method, which was originally proposed by Dion *et al.*[33] and further developed by Thonhauser [34], Michaelides, [35, 36] Román-Pérez [37] and some others. Exchange functional, optB88-vd, [36, 37] were chosen, which were reported to be reasonably accurate for surface adsorption calculations.[38, 39] Brillouin zone integration was accomplished using a  $2\times 2\times 1$  Monkhorst-Pack k-point mesh. All the adsorption geometries were optimized using a force-based conjugate gradient algorithm, while transition states (TSs) were located with a constrained minimisation technique.[40-42]

Three different surfaces were considered in this work, namely the close-packed platinum surface (Pt(111)), platinum on tin oxide ( $Pt/SnO_2$ ), and platinum on reduced tin oxide ( $Pt/SnO_{2-x}$ ).

For the modelling of Pt(111), a typical surface model with a periodic four-layer  $p(4\times4)$  model with the 2 lower layers fixed and 2 upper layers relaxed were used. For the modelling of platinum on tin oxide, we used a global optimization method, namely the particle swarm optimization (PSO), to obtain the most stable structures of cluster-oxide structures. Comparing to some previous modelling of bi-component systems,[43, 44] this global optimization algorithm can provide a much more realistic and accurate illustration of cluster and interface structures, which may be of great importance in the selective hydrogenation of benzoic acid. In this work, the PSO were carried out using the CALYPSO code,[45-47] which is a power tool to get the stable structures at given external conditions. The unreduced tin oxide was modelled with a six-layer model with 3 upper layers relaxed and 3 lower layers fixed, while the reduced surface was modelled by removing the bridge oxygen of unreduced tin oxide. For both Pt/SnO<sub>2</sub> and Pt/SnO<sub>2-x</sub>, Pt clusters with twelve platinum atoms were chosen, and the structures of cluster and interface were obtained using PSO. Twenty

optimization generations were calculated with sixteen surfaces in each generation. Thus, overall 320 structures were examined for both systems, and the most stable surfaces were chosen.

### 3 Results and discussion

#### 3.1 Hydrogenation of benzoic acid

The hydrogenation of benzoic acid over Pt/SnO<sub>2</sub> gave excellent selectivity to benzyl alcohol with selectivity of 97% at 98% conversion of benzoic acid (Figure 1). This reaction was performed at 190 °C and 30 bar H<sub>2</sub> which are considerably milder reaction conditions for hydrogenation of benzoic acid than have been previously reported.[18] Trace amounts of intermediate hydrogenation product benzaldehyde was also detected (Figure 1b) with a maximum of 16% selectivity to benzaldehyde observed only at the very start of the reaction while esterification product benzyl benzoate was only formed in trace amounts <1% after 24 hour of reaction. Under these reaction conditions, Pt/SnO<sub>2</sub> was found to be reusable with no significant change in the conversion of benzoic acid or the selectivity to benzyl alcohol observed for three recycle reactions with a reduction at 200 °C, 30 bar H<sub>2</sub> for 1 hour performed before each recycle reaction (Figure S1). There was no activity observed when the catalyst was recycled without the reduction step.

Interestingly, hydrogenation of the aromatic ring was not observed over Pt/SnO<sub>2</sub> under any of the reactions conditions used in this study. In addition, when benzene was used as the substrate, no hydrogenation was observed. Adsorption/reaction of aromatic rings was hindered on Pt when supported on SnO<sub>2</sub>. The promoting effect of SnO<sub>2</sub> as the support was also highlighted by the differing reactivities/selectivities that were observed for Pt supported on carbon and alumina. For a commercial Pt/C catalyst, lower activity compared to Pt/SnO<sub>2</sub> was observed with only 24% conversion after 24 hours of reaction. The major product of the reaction over Pt/C was cyclohexane carboxylic acid with selectivities of 81.4% to cyclohexane carboxylic acid, 14.9% to benzyl alcohol and 3.7% to cyclohexylmethanol (Figure S2). Even lower activity was observed for reaction over a 5%Pt/Al<sub>2</sub>O<sub>3</sub> catalyst where only 3% conversion was observed after 24 h of reaction at 190 °C and 30 bar H<sub>2</sub> (Figure S3)

and reaction over the  $SnO_2$  support alone gave only 2% conversion in 24 h of reaction likely due to lack of activation of hydrogen without platinum (reaction at 190 °C and 30 bar H<sub>2</sub>). The activity for acid carbonyl hydrogenation is clearly promoted by an interaction between Pt and  $SnO_2$ .



Figure 1: (a) reaction profiles for the hydrogenation of benzoic acid over Pt/SnO<sub>2</sub> at 190 °C and 30 bar H<sub>2</sub>, catalyst (200 mg) pre-reduced *in situ* at 200 °C and 30 bar H<sub>2</sub> for 1 h before reactions; • benzoic acid, • benzyl alcohol and • benzaldehyde with  $\bigcirc$  showing the sum of the concentration of reagent and products through the reaction (b) %selectivity *vs.* %conversion for hydrogenation of benzoic acid for reactions at 190 °C/30 bar (closed symbols) and 150°C/15 bar (hollow symbols).

The acid carbonyl group activation ability of this catalyst was further highlighted by the formation of benzyl alcohol in a reaction performed at only 150 °C and 15 bar H<sub>2</sub>. However, at these milder conditions, an effect of adsorption was observed with comparable initial rates of removal of the benzoic acid observed for the reactions under H<sub>2</sub> and N<sub>2</sub>. However, the formation of benzyl alcohol was only observed for the reaction under H<sub>2</sub> (Figure S4) and at a lower rate than the removal of benzoic acid indicating that the latter is dominated by adsorption at these milder conditions.

Variation of the reaction pressure partial pressures of  $H_2$  of 5, 10 and 20 bar (total reaction pressures of 15, 20 and 30 bar) showed an increase in initial rate of production of benzyl alcohol from 0.028 to 0.048 mmol dm<sup>-3</sup> min<sup>-1</sup> with increasing pressure. The initial rates of reaction were determined from the formation of benzyl alcohol as opposed to the conversion of benzoic acid due to the strong adsorption

observed in the initial period of the reaction. The order of reaction with respect to hydrogen was determined from a plot of ln(initial rate) against  $ln(H_2 \text{ pressure})$  and was found to be of fractional order with a value of 0.4 (Figure 2).

The initial rate of reaction was also found to vary with the concentration of benzoic acid in the reactor (0.001 to 0.003 moles) with the rate increasing with concentration. The order of reaction with respect to benzoic acid was found to be 0.8 (Figure 3).



Figure 2: (a) initial rate of reaction (formation of benzyl alcohol) over  $Pt/SnO_2$  at 190 °C and 5 - 20 bar partial pressure of H<sub>2</sub>, catalyst (100 mg), 0.002 mol benzoic acid, 40 ml dioxane; and (b) ln(initial rate) against ln(H<sub>2</sub> partial pressure). The catalyst was pre-reduced *in situ* at 200 °C and 30 bar H<sub>2</sub> for 1 h before reactions.



Figure 3: (a) initial rate of reaction (formation of benzyl alcohol) over  $Pt/SnO_2$  at 190 °C and 20 bar partial pressure of H<sub>2</sub>, catalyst (100 mg), varying the concentration of benzoic acid between 0.001 and 0.003 mol, 40 ml dioxane and (b) ln(initial rate) against ln(benzoic acid concentration). The catalyst was pre-reduced *in situ* at 200 °C and 30 bar H<sub>2</sub> for 1 h before reactions.

### 3.2 Catalyst characterisation

Characterisation of the properties of the Pt/SnO<sub>2</sub> catalyst (Table S1) was performed and compared to that of Pt/Al<sub>2</sub>O<sub>3</sub> which was inactive for the hydrogenation of benzoic acid. While Pt/SnO<sub>2</sub> has a significantly lower surface area than Pt/Al<sub>2</sub>O<sub>3</sub> (9.3 m<sup>2</sup> g<sup>-1</sup> and 235 m<sup>2</sup> g<sup>-1</sup> respectively) TEM analysis showed comparable Pt particle sizes of 1-2 nm for both catalysts (Figures S5-S6). XRD of the catalysts showed only peaks due to the supports which corroborates the small size of the Pt particles observed by TEM (Figure S7). This indicates that the surface area and particle size effects/dispersion are not the main influence on the activity of these catalysts and again suggests that an interaction between the metal and the support is important for the activity of Pt/SnO<sub>2</sub>.

TPR of Pt/Al<sub>2</sub>O<sub>3</sub> and PtSnO<sub>2</sub> catalysts are shown in Figure 4. For PtSnO<sub>2</sub>, the main reduction features occurred between 200-400 °C due to reduction of PtO<sub>x</sub> strongly interacting with the support and also possibly some partial reduction of SnO<sub>2</sub> most likely at the interface with the Pt nanoparticles (Figures 4 and S8).[48, 49] A small reduction feature at much lower reduction temperatures (below 100 °C) was also observed which could be due to reduction of PtO<sub>x</sub> weakly interacting with the Pt/SnO<sub>2</sub> support. Bulk SnO<sub>2</sub> reduction occurred above 500 °C for Pt/SnO<sub>2</sub> while for the support alone, bulk reduction of SnO<sub>2</sub> occurred above 650 °C (Figure S8). The reduction of PtO<sub>x</sub> are observed to be complete at temperatures below 300 °C with the main reduction peak occurring at 110 °C, showing the weaker interaction of Pt with the alumina compared to the tin dioxide support.



Figure 4: TPR of Pt/SnO<sub>2</sub> (dashed line) and Pt/Al<sub>2</sub>O<sub>3</sub> (solid line).

To probe the oxidation state of the Pt and Sn in Pt/SnO<sub>2</sub>, XPS analysis was performed on the fresh Pt/SnO<sub>2</sub> catalyst and after reduction at 200 °C (1 mbar of H<sub>2</sub> pressure for 15 min). XP spectra of the Pt4f region for Pt/Al<sub>2</sub>O<sub>3</sub> showed only a single Pt species with Pt4f<sub>7/2</sub> peak at 73.4 eV due to Pt(II) species (Figure S9). For Pt/SnO<sub>2</sub>, Pt was predominantly in an oxidised state with Pt4f<sub>7/2</sub> peaks at 74.7 eV and 72.8 due to Pt(IV) and Pt(II) species with a minor contribution due to metallic Pt at 71.2 eV also observed (Figure 5)[50, 51] which has also been reported for PtSn/C catalysts.

In order to investigate the effect of the reduction procedure on the Pt/SnO<sub>2</sub> catalyst, NAP-XPS was employed to simulate the reduction procedure utilising an in-situ approach preventing ambient exposure of the sample prior to analysis which can alter the true chemistry of the reduced surface. Figure 5 displays the Pt4f regions following the reduction where a dramatic change in peak shape was noted for the Pt4f profile with only metallic Pt observed in the sample surface after reduction.

In addition to a change in the Pt4f profile following reduction, a change was also noted in the Sn3d profile as displayed in Figure 6. A single doublet within the Sn3d window was noted for the fresh catalyst upon loading, consistent with a SnO<sub>2</sub> state (binding energy for Sn3d<sub>5/2</sub> of 486.9 eV). Following the reduction,

two key features are noted for the Sn3d spectrum. Firstly, a shift to higher binding energy is noted for the oxidised Sn peaks (~ 0.3 eV) relative to the as loaded state. This shift in B.E. could be explained as a result of band bending, as seen in previous SnO<sub>2</sub> studies via XPS [52].

Secondly, a shoulder feature emerges (binding energy for  $\text{Sn}3d_{5/2}$  of 485.6 eV) from the main peak doublet with a separation of 1.4 eV on the lower binding energy side from the main feature, consistent with the shift separation expected between  $\text{SnO}_2$  and Sn metal. Previous studies of metallic Pt deposited on a  $\text{SnO}_2$  surface by Körber et al have shown that metallic platinum can reduce the  $\text{SnO}_2$  surface to metallic Sn [53] and formation of metallic tin has also been observed for a range of Pt-Sn catalysts with Sn  $3d_{5/2}$  peaks at 485.6 eV reported to be in the range for metallic tin in an alloy phase [54]. The proportion of metallic tin after reduction was below 10% highlighting that tin is predominantly in an oxidised state even after reduction at 200 °C.

The presence of both metallic tin and metallic platinum could suggest formation of alloy phases which have been reported for Pt/SnO2 and Pt-Sn/metal oxide catalysts. XRD of Pt/SnO2 after reduction at 170/200 °C showed formation of a PtSn phase; [21] however, reduction of a 20%Pt/SnO<sub>2</sub> catalyst at 200 °C did not show formation of intermetallic compounds by XRD [48]. Interestingly both these studies showed higher reduction temperatures (250 and 400 °C respectively) to generate tin rich alloy phases (PtSn<sub>2</sub> and PtSn<sub>4</sub>) with lower activity observed following this high temperature reductive treatment. However, study of crotonaldehdye hydrogenation over pure Pt(111) and model Sn/Pt(111) alloy surfaces showed only an enhancement in the activity for the alloy surfaces compared to the Pt(111) surface with no change in selectivity [55]. This suggests that alloy formation alone cannot account for the enhancements in selectivity for C=O hydrogenations with Pt-support interactions as well as Pt-Sn interactions required for control of the activity and selectivity which are likely influenced by catalyst preparation method as well as the temperature of reduction. The activation of C=O bonds by ionic (oxidic) tin species has been reported for PtSn catalysts prepared by surface organometallic reactions which have been shown to be active and selective for hydrogenation of furfural to furfural alcohol[56] and cinnamaldehyde to cinnamyl alcohol

[57]. For these catalysts, Pt-Sn alloy phases and ionic tin species were observed on the catalyst with ionic tin proposed to activate the C=O bond of the aldehydes to hydrogenation.



Figure 5: XP spectra of the Pt 4f region for  $Pt/SnO_2$  as loaded and after reduction.



Figure 6: XP spectra of the Sn 3d region for  $Pt/SnO_2$  as loaded and after reduction.

CO pulse chemisorption and was performed to study the effect of reduction temperature on the CO adsorption capacity of Pt. For Pt/Al<sub>2</sub>O<sub>3</sub> reduced at 200 °C, CO pulse chemisorption gave a dispersion of 55% which decreased to 16% following reduction at 350 °C which is likely due to sintering of the Pt particles. For the Pt/SnO<sub>2</sub> catalyst, significantly lower adsorption of CO was observed (calculated dispersion was only 0.72%) following reduction at 200 °C while no CO uptake occurred when reduced at 350 °C. The lower chemisorption ability of Pt when supported on SnO<sub>2</sub> compared to Al<sub>2</sub>O<sub>3</sub> is indicative of the interaction between Pt and Sn which could be due to dilution effects from alloy formation and/or migration of SnOx species onto the Pt surface.

DRIFT spectroscopy was also utilised to probe the electronic state of Pt in the  $Pt/SnO_2$  catalyst. The adsorption of CO at room temperature following reduction at temperatures between 100 and 350 °C was performed over Pt supported on  $SnO_2$  and compared to Pt supported on  $Al_2O_3$ .

For Pt/SnO<sub>2</sub>, in the temperature region where reduction of PtO<sub>x</sub> and partial reduction of interfacial SnO<sub>2</sub> occurs (200-400 °C from TPR), the chemisorption ability of Pt for CO was significantly modified (Figure 7). For reduction below 200 °C, weak Pt-CO bands were observed with a band at 2086 cm<sup>-1</sup> for T<sub>red</sub> of 100 °C, 2080 cm<sup>-1</sup> for T<sub>red</sub> of 150 °C shifting to 2075 cm<sup>-1</sup> for T<sub>red</sub> of 250 °C. These bands are assigned to CO linearly adsorbed on terrace sites of Pt particles.[58] No bands due to CO adsorption on the support were observed under any conditions used herein.

The shifting of the Pt-CO band from 2086 - 2075 cm<sup>-1</sup> could be a result of restructuring of the Pt nanoparticle with more coordinatively unsaturated sites forming or the generation of electron rich Pt sites (increased backbonding into CO antibonding orbitals weakening the CO bond and red-shifting the Pt-CO band) following reduction at 200 °C.[59] Alternatively, the red shift (2086 to 2075 cm<sup>-1</sup>) could be a result of a geometric effect where alloy formation or migration of SnO<sub>2</sub>/SnO<sub>2-x</sub> species onto the Pt could block sites for CO

adsorption giving a lower coverage of CO and a reduction in dipole-dipole coupling which shifts the band position to lower wavenumbers.



Figure 7: DRIFT spectra recorded under 2% CO in Ar at room temperature over  $Pt/SnO_2$  following reduction in 10% H<sub>2</sub>/Ar between (a) 100 and 200 °C and (b) 200 and 350 °C.

Following reduction at 200 °C, the intensity of the linear Pt-CO band at 2075 cm<sup>-1</sup> increased and a new linear Pt-co band was observed at 2040 cm<sup>-1</sup> suggesting modification of the platinum surface with reduction of the catalyst. Similar

spectra were observed for Pt-Sn/TiO<sub>2</sub> catalysts with bands at 2072 cm<sup>-1</sup> with a shoulder at 2040 cm<sup>-1</sup> [60]. A band at 2050 cm<sup>-1</sup> has also been observed for Pt-Sn alloyed catalysts[58, 60] and assigned to CO adsorbing on Pt sites belonging to a Pt-Sn phase. In the study of Moscu et al. it was highlighted that the PtSn phases could be intermetallic compounds such as PtSn or Pt<sub>3</sub>Sn or a random alloy and interestingly, they showed that the alloy phases could segregate and be regenerated with variation in the temperature. Under the CO/H<sub>2</sub> feed at temperatures above 175 cm<sup>-1</sup>, a single band for CO adsorbed on Pt-Sn species was observed between 2054-2045 cm<sup>-1</sup> while at lower temperatures (<175 °C) segregation of the Pt-Sn alloy phases occurred with the Pt-CO band position shifting to 2071 cm<sup>-1</sup> indicating adsorption of CO on essentially pure Pt sites.

Herein, the formation of the band at 2040 cm<sup>-1</sup> between 150-200 °C reduction temperature, could be due to CO adsorption on a Pt-Sn alloy phase which corroborates the study of Liberková and Touroude [21] where Pt-Sn alloy phases were observed to form at 170 °C.

The Pt-CO band at 2075 cm<sup>-1</sup> (CO adsorbed on essentially pure Pt sites) continued to shift to lower wavenumbers upon increasing the temperatures until a reduction of 350 °c wherein, Pt-CO bands were no longer detected. DRIFT spectra of the adsorption of CO on Pt/SnO<sub>2</sub> show that both Pt and Pt-Sn sites are present on the surface of the catalyst with reduction of the catalyst above 200 °C resulting in significant perturbation of the chemisorption ability of the catalyst which is likely due to encapsulation of platinum by SnO<sub>2</sub>/SnO<sub>2-x</sub> species or formation of tin-rich alloy phases.[48, 61].

The characterisation of the catalysts highlights that the temperature of reduction for  $Pt/SnO_2$  can significantly alter the interaction between Pt and Sn. However, all the techniques used to characterise the catalysts were performed under a flow of  $H_2$  (gas phase reduction) which differs from the in-situ reduction in the liquid phase performed in the catalytic activity tests. As the reduction is essential for the state of the catalyst, the hydrogenation of benzoic acid after gas phase flow reductions at 200 °C (performed in the autoclave without solvent) and at 400 °C (ex-situ reduction in a furnace) were also performed.

For the flow reduction at 200 °C, the conversion of benzoic acid was slightly lower which could be due to mass transfer limitation of H<sub>2</sub> to the catalyst for flow in the Parr reactor (no solvent/mixing) (Figure S10). Importantly, the same selective formation of benzyl alcohol was observed which suggests that the active state of Pt/SnO<sub>2</sub> was comparable following both reductive treatments at 200 °C.

For the reduction of Pt/SnO<sub>2</sub> at 400 °C, the hydrogenation activity of Pt/SnO<sub>2</sub> was significantly reduced with only 3.5% conversion after 24 h of reaction at 190 °C and 30 bar H<sub>2</sub> forming benzyl alcohol, benzaldehyde and benzyl benzoate. Figure 11 shows the %Selectivity *vs.* %Conversion profile for this reaction where slow conversion of benzaldehyde to benzyl alcohol is observed (%S = 73%, 16% and 11% to benzyl alcohol, benzaldehyde and benzyl benzoate after 24 h of reaction). Reduction at 400 °C has significantly impaired the activity of the catalyst compared to the standard 200 °C reduction which is likely related to decreased hydrogen dissociation when Pt is encapsulated by SnO<sub>x</sub>.

The Pt assisted reduction of  $SnO_2$  is essential in providing the activity of this catalyst. The formation of an alloy phase/ migration of  $SnO_x$  onto Pt could block sites for hydrogenation of the aromatic ring with oxidised tin species  $(SnO_x)$  likely at the periphery of the Pt nanoparticle proposed to activate the acid carbonyl group for hydrogenation.

#### 3.3 DFT calculations

To probe whether partially reduced  $(SnO_x)$  species can activate the C=O bond for hydrogenation, DFT calculations of the mode and energy of adsorption of benzoic acid on Pt(111) and Pt supported on tin dioxide were performed.

To model the platinum on tin dioxide, a global optimization method was used, namely particle swarm optimization (PSO), to obtain the most stable Pt-SnO<sub>2</sub> cluster-oxide structures (Table S2 and Figure S12). In comparison with previous modelling of bi-component systems, [43, 44] this global optimization

algorithm can provide a much more realistic and accurate illustration of cluster and interface structures, which is required in order to study catalytic systems where the activity is related to support-metal interactions.

For each system, the adsorption energy was calculated for benzoic acid adsorption though either the aromatic ring or the acid carbonyl group (Table 1). For the Pt(111) surface,  $\pi$  adsorption through the aromatic ring was found to be considerably more favoured than  $\sigma$  adsorption through the acid carbonyl group with adsorption energies of -1.25 and -0.89 eV respectively (Figure 8). The adsorption energy of benzoic acid on Pt/SnO<sub>2</sub> showed a comparable trend to that of benzoic acid on Pt(111) with the  $\pi$  interaction favoured with adsorption energies of -1.25 and -0.89 eV for Pt(111), and -2.02 and -1.28 eV for Pt/SnO<sub>2</sub> (Figure 8 and S13). The favoured  $\pi$  mode of adsorption indicates that hydrogenation of the aromatic ring would be the expected pathway over both these surfaces; however, this was not observed experimentally. This suggests that reduction to the metal alone cannot produce an active catalyst therefore reduction of the support was also considered in the modelling of benzoic acid adsorption in this catalytic system.

The adsorption of benzoic acid on a reduced Pt/SnO<sub>2-x</sub> surface was modelled by removing the bridging oxygen from tin dioxide. This partial support reduction resulted in a change in the most stable Pt cluster structure and interestingly, a switch in the favoured mode of adsorption of benzoic acid with the  $\sigma$  adsorption mode now more favourable than the  $\pi$  interaction with binding energies of -0.98 and -0.74 eV, respectively (Figures 8 and S13). Reduction of the tin dioxide led to a significant weakening of the  $\pi$  mode of adsorption of benzoic acid compared to when adsorbed on the Pt(111) and Pt/SnO<sub>2</sub> (unreduced tin dioxide) surfaces. Modelling of benzoic acid adsorption on platinum with a strong interaction with the tin dioxide support resulted in activation of the acid carbonyl group in favour of the aromatic ring and showed that partial reduction of SnO<sub>2</sub> could influence the reaction selectivity in line with the activity data and catalyst characterisation results.

	Adsorption energy / eV	
	$\sigma$ adsorption	$\pi$ adsorption
Pt(111)	-0.89	-1.25
Pt/SnO <sub>2</sub>	-1.28	-2.02
Pt/SnO <sub>2-x</sub>	-0.98	-0.74

Table 1: DFT calculated adsorption energy for benzoic acid on Pt(111), unreduced  $Pt/SnO_2$  and partially reduced  $Pt/SnO_{2-x}$ 



Figure 8: Favoured mode of adsorption of benzoic acid over (a) Pt(111), (b)  $Pt/SnO_2$ , unreduced catalyst, and (c)  $Pt/SnO_{2-x}$  reduced surface. Oxygen, carbon and hydrogen atoms are in red, grey, and white, respectively.

### 3.4 Hydrogenation of benzoic acid over Pt/Al<sub>2</sub>O<sub>3</sub>

DFT calculations on Pt(111) and Pt on SnO<sub>2</sub> (without reduction) showed that benzoic acid adsorption occurs through the aromatic ring which has also been reported experimentally for Pt(111).[62] It is interesting therefore, that no hydrogenation activity was observed over the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst as a degree of activity towards cyclohexane carboxylic acid could be expected as was observed over Pt/C (Figure S2). To investigate this, *in-situ* ATR spectroscopy was used to study the adsorption of benzoic acid over Pt/Al<sub>2</sub>O<sub>3</sub>.

A Pt/Al<sub>2</sub>O<sub>3</sub> layer, pre-reduced under a flow of H<sub>2</sub>-saturated dioxane at 90 °C was exposed to a 0.1 M benzoic acid in dioxane solution at room temperature (Figure 9 and S15). In the spectra over both the catalyst (Figure 9), and the alumina support alone (Figure S16) adsorption of benzoic acid formed bidentate benzoate species from dissociative adsorption of benzoic acid on alumina. Bands due to the benzoate species were observed at 1604, 1552 and 1397 cm<sup>-1</sup> and assigned to a ring stretch of the benzoate and the carboxylate asymmetric and symmetric stretches respectively.[63] Bands at 1723 cm<sup>-1</sup> and 1239 cm<sup>-1</sup> are due to liquid phase benzoic acid dissolved in the dioxane.[64] In addition, a band at 2053 cm<sup>-1</sup> was observed and assigned to CO linearly adsorbed on metallic Pt. A band at 2053 cm<sup>-1</sup> was also observed following adsorption of CO on a pre-reduced Pt/Al<sub>2</sub>O<sub>3</sub> catalyst layer (Figure S17). The formation of CO during benzoic acid adsorption over Pt/Al<sub>2</sub>O<sub>3</sub> could result from decomposition or decarbonylation reactions. Decarbonylation of benzyl alcohol[65, 66] and benzaldehyde[67] has been reported over Pd/Al<sub>2</sub>O<sub>3</sub> in the liquid phase at comparable temperatures to those used in this ATR study. Ferri et al. reported the desired oxidation of benzyl alcohol to benzaldehyde to be insensitive to specific sites on the Pd particles; however, decarbonylation was found to occur over hollow sites on terraces of the Pd nanoparticles (Pd(111))[68] with the presence of oxygen in the feed reducing the deactivating effect of CO adsorbed on Pd for this reaction.

Under the hydrogenation conditions used within this study, CO (and possibly hydrocarbon fragments from decomposition of benzoic acid/benzaldehyde) could remain adsorbed on the Pt surface poisoning the catalyst for subsequent adsorption of benzoic acid resulting in the low activity observed experimentally over Pt/Al<sub>2</sub>O<sub>3</sub>. The reducible nature of the tin dioxide support is able to promote both the activity and selectivity to the acid carbonyl hydrogenation of benzoic acid suppressing hydrogenation of the aromatic ring and side reactions/decomposition.



Figure 9: *In-situ* ATR spectra recorded during adsorption of 0.1 M benzoic acid in dioxane over Pt/Al<sub>2</sub>O<sub>3</sub> at room temperature (3 min of exposure). Pt/Al<sub>2</sub>O<sub>3</sub> was pre-reduced in a flow of H<sub>2</sub>-saturated dioxane at 90 °C. Bands due to dioxane solvent have been subtracted. \* Bands due to bidentate benzoate species adsorbed on alumina:

### 4 Conclusions:

In conclusion, platinum supported on tin dioxide is active and highly selective for the formation of benzyl alcohol from benzoic acid under extremely mild reaction conditions in the liquid phase. The interaction between Pt and SnO<sub>x</sub> provides activation of the acid carbonyl group with the catalysts showing no activity for aromatic ring hydrogenation as further evidenced by the inactivity for hydrogenation of benzene. Characterisation of the catalyst shows a degree of reduction of the SnO<sub>2</sub> support following treatment under H<sub>2</sub> at 200 °C however, tin is present predominantly as an oxidised species although with the formation of both metallic Pt and Sn, alloy phases could also be generated. DFT suggests that interaction between the Pt and SnO<sub>x</sub> can weaken the strength of adsorption of the aromatic ring of benzoic acid rendering its adsorption unfavourable relative to the acid carbonyl group. The switch in adsorption mode with partial reduction of the tin dioxide corroborates the observed

reaction selectivity with ring hydrogenation observed over Pt/C, ring adsorption and decomposition observed over Pt/Al<sub>2</sub>O<sub>3</sub> and acid carbonyl group adsorption and hydrogenation over Pt/SnO<sub>2</sub> with excellent selectivity to benzyl alcohol.

### Author contribution

The contribution of the authors is as follows:

Preparation and characterisation of catalysts (BET, XRD, ICP, TPR, CO chemisorption): Xiaohan Chen and Richard Morgan

Activity testing: Xiaohan Chen and Helen Daly

DFT calculations: Ziyun Wang and Peijun Hu

XPS and NAP-XPS data collection and analysis: Rebecca Taylor, Conor Byrne and Alex Walton

DRIFTS and ATR data collection and analysis: Helen Daly

TEM: Mathew Smith

Project ideas and discussion of results: Chris Hardacre, Helen Daly, Haresh Manyar and Robbie Burch

Writing the paper: Xiaohan Chen, Ziyun Wang, Helen Daly and Chris Hardacre

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